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FILING DATE.

APPLICATION NUMBER: 60/360,999

FILING DATE: March 01, 2002

RELATED PCT APPLICATION NUMBER: PCT/US03/05771



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## PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

Express Mail Label No. ET931353912US

### INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
GRACIELA BEATRIZ	BLANCHET-FINCHER	GREENVILLE, DELAWARE

☒ Additional inventors are being named on the PAGE 2 separately numbered sheets attached hereto

### TITLE OF THE INVENTION (500 characters max)

LASER PRINTING OF CONDUCTIVE POLYANILINE WITH ADDITIVES

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### ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification Number of Pages

19

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☒ Drawing(s) Number of Sheets

5

☐ Other (specify)

☐ Application Data Sheet. See 37 CFR 1.76

### METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

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04-1928

FILING FEE  
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160

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☐ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: \_\_\_\_\_

Respectfully submitted,

SIGNATURE

*Barbara C. Siegel*

Date

03/01/02

TYPED or PRINTED NAME

BARBARA C. SIEGELL

REGISTRATION NO.

30,684

(If appropriate)

Docket Number

CL2011 US PRV

TELEPHONE 302.992.4931

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This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C., 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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FENG	GAO	WILMINGTON, DELAWARE

2010E0166609E09

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# FEE TRANSMITTAL for FY 2002

Patent fees are subject to annual revision

☐ Applicant Claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$) 160

## Complete if Known

Application Number	UNKNOWN
Filing Date	MARCH 1, 2002
First Named Inventor	GRACIELA BEATRIZ BLANCHET-FINCHER
Examiner Name	UNKNOWN
Group / Art Unit	UNKNOWN
Attorney Docket No	CL2011 US PRV

## METHOD OF PAYMENT (check all that apply)

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E. I. du Pont de Nemours and Company

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## FEE CALCULATION

### 1. BASIC FILING FEE

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
101	740	201	370	Utility filing fee	
106	330	206	165	Design filing fee	
107	510	207	255	Plant filing fee	
108	740	208	370	Reissue filing fee	
114	160	214	80	Provisional filing fee	160

SUBTOTAL (1) (\$) 160

### 2. EXTRA CLAIM FEES

Total Claims	-20	=	0	X	18	=	0
Independent Claims	-3	=	0	X	84	=	0
Multiple Dependent				X	280	=	0

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
103	18	203	9	Claims in excess of 20	
102	84	202	42	Independent claims in excess of 3	
104	280	204	140	Multiple dependent claim, if not paid	
109	84	209	42	** Reissue independent claims over original patent	
110	18	210	9	** Reissue claims in excess of 20 and over original patent	

SUBTOTAL (2) (\$) 0

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## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension for reply within second month	
117	920	217	460	Extension for reply within third month	
118	1,440	218	720	Extension for reply within fourth month	
128	1,960	228	980	Extension for reply within fifth month	
119	320	219	160	Notice of Appeal	
120	320	220	160	Filing a brief in support of an appeal	
121	280	221	140	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,280	241	640	Petition to revive - unintentional	
142	1,280	242	640	Utility issue fee (or reissue)	
143	460	243	230	Design issue fee	
144	620	244	310	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Processing fee under 37 CFR 1.17(q)	
126	180	126	180	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	740	246	370	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	740	249	370	For each additional invention to be examined (37 CFR § 1.129(b))	
179	740	279	370	Request for Continued Examination (RCE)	
169	900	169	900	Request for expedited examination of a design application	

Other fee (specify) \_\_\_\_\_

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SUBTOTAL (3)

(\$) 0

## SUBMITTED BY

Name (Print/Type)		Registration No. Attorney/Agent		Telephone	
BARBARA C SIEGELL		30,684		302 992 4931	
Signature		Date		MARCH 1, 2002	

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## **FIELD OF THE INVENTION**

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backbone, said polymer optionally doped with excess organic protonic acid with 3 to 30 carbons such that there are between 0.15 and 1.0 molecules of the excess organic protonic acid for each nitrogen in the polyaniline;

5 the composition further comprising one or more components selected from the group of:

- b) surfactant at a concentration of between 0.05% and 0.5% by weight;
- c) plasticizer at a concentration of between 1% and 30% by weight; and
- 10 d) a second macromolecule at a concentration of between 1% and 30% by weight;

wherein the doped polymer of (a) comprises not less than about 70% by weight of the solids in the composition.

15 The invention also concerns the above composition further comprising carbon nanotubes at a concentration of between 0.5% to 13% by weight.

Also disclosed is a process comprising:

- a) coating the above composition, in a solvent, on a transparent donor element;
- 20 b) contacting the transparent donor element with a receiver element such that the coating lies between the transparent donor element and the receiver element; and
- c) irradiating the coating through the transparent donor element with a laser to transfer the coating on the donor element to the receiver.

Preferred solvents for use in the above process consist of xylenes, toluene, cyclohexane, chloroform, isopropanol, 2-butoxyethanol and mixtures thereof.

30 A further embodiment of the invention is the above process wherein the laser irradiating step forms a pattern on the receiver element.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the conductivity (S/cm) as a function of laser power.

Figure 2 shows conductivity over watts. Excess DBSA reduces the film conductivity.

35 Figure 3 shows the conductivity of the transferred solid strips as a function of the laser transfer power.



than insulating properties such that they could be used in active electronic devices.

Tailoring electrical properties of polymers has been achieved utilizing three different strategies:

- 5        1) Modifying the intrinsic bulk properties by altering the chemical composition and structure of the starting material
- 2) Altering the properties of the polymer at the molecular level by incorporating dopants, which may form charge transfer complexes with the host polymer.
- 10      3) Incorporating microscopic pieces such as metal flakes, carbon-black particulate into the host polymer to form conducting polymers.

Although, the second route clearly provides the most efficient pathways to polymeric synthetic metals, materials tend to exhibit lack of stability under ambient conditions. In the case of polyacetylene, poly(1,6-heptadiyne) and polypropyne the un-doped polymers are unstable in oxygen. Although poly-p-phenylene, poly-p-phenylene oxide and poly-p-phenylene sulfide are stable in oxygen they can only be doped with powerful acceptors such as  $\text{AsF}_5$  and once doped they are susceptible to rapid hydrolysis under ambient conditions. Although polypyrrole is stable under ambient conditions it lacks some of the other desirable characteristics, most notably variable conductivity.

Alternatively, more modest conductivity values (0.001 S/cm) can be achieved by filling inert polymers with conductors. Conductivities of  $10^{-10}$  to  $10^{-1}$  S/cm are readily achieved and can be tailor into the specifications. The electrical conductivity depends upon filler loading and there is a steep dependence upon filler load over a short range above a critical level (percolation threshold). Since high levels of filler loading 10-40% are employed to achieve high conductivities, polymer process ability is severely hindered. Typical fillers are PAN- derived C fibers, metallized glass fibers, Al flakes, and carbon black. Typical loading and resulting conductivities are shown in Table 1.



Table 1

Composite	Conductivity (S/cm)
Polycarbonate (PC)	$10^{-16}$
PC + 20% Al flake	$10^{-15}$
PC + 30% Al flake	1
PC + 10% PAN carbon fiber	$10^{-8}$
PC+ 40% PAN C fibers	$10^{-2}$
Nylon 6,6 (N-6,6)	$10^{-14}$
N-6,6 + 40% pitch C fiber	$10^{-4}$
N-6,6 + 40% PAN C fiber	1

5 In contrast, typical synthetic metals such as polyacetylene, polyphenylene, and polyphenylene sulfide, can exhibit conductivities ranging from  $10^2$ - $10^3$  s/cm in the metallic regime. However, since these values are obtained via strong oxidizing or reducing reaction materials, they tend to be not stable at ambient conditions limiting practical applications.

10 The search for environmentally stable synthetic metals led to considerable effort in polyaniline (PANI). Although these materials have lower conductivity in the metallic state they appear to also have significant de-localization in the polymer backbone but unlike other conducting polymers they are stable in air indefinitely. In particular, the emeraldine

15 base form of polyaniline can be doped to the metallic conducting regime by dilute non-oxidizing aqueous acids such as HCl to yield an emeraldine salt that exhibits metallic conductivity but is air stable and inexpensive to produce in large quantities. The emeraldine form of polyaniline is believed to show high conductivity because of the extensive conjugation of the

20 backbone. Unlike all other conjugated polymers, the conductivity of the material depends on two variables rather than one, namely the degree of oxidation of the PANI and the degree of protonation. However, most polyanilines have  $10^2$ - $10^6$  lower conductivity than polyacetylene. The highest conductivity PANI's are those cast from solutions of PANI

25 camphosulfonate (PANI-CSA) in m-cresol. Conductivities of approximately  $10^2$  S/cm are observed. This is about two order of magnitude higher than PANI's protonated with mineral acids which range

from  $10^{-1}$  to  $10^1$  S/cm. Although PANI-CSA has sufficiently high conductivity, the use of m-cresol with a boiling point of  $203^\circ$  severely limits its use in plastic electronics where substrates, such as Mylar®, are not stable at such elevated temperatures.

5        Achieving stable polymeric materials with metallic conductivities that are processable and stable at ambient conditions is important for the use of conducting polymers in electronic applications. During the past decade, there has been a growing interest in developing thin film field effect transistors (TFT) using inexpensive and easily processable organic  
10       materials. In principle, organic materials have greater flexibility and easier tunability relative to the silicon based counterparts. Considerable activity has been focused on the development of semiconductor materials with high mobilities for applications in TFT's due to vast variety of organic materials available. Poly(alkylthiophenes), oligothiophenes, pentacene,  
15       phthalocyanines are just a few examples of such semiconductors. However, the conducting layer in such devices has typically utilized metals.

20       The use of PANI's in organic electronics requires the ability to pattern the material with high resolution. If the organic conductor is to be used as the source and drain in plastic transistors it requires imaging the source and drain conducting lines ranging from 5 to 100 microns in width with a separation between source and drain lines of 1-20 microns. Patterning of the conducting layer through a laser thermal transfer process will be described in detail for such applications. If imaging is performed via  
25       a transfer technique such as thermal imaging, the resolution of the image lines as well as device performance is controlled by the adhesion of the transfer film onto either a dielectric or a semiconducting layer. In addition, the conductivity of the organic conducting film must be preserved throughout the imaging process. This invention shows that the formulation  
30       of organic conductors suitable for high-resolution imaging can be achieved by tuning the adhesion of the transfer organic conducting layer on to the receiver layer. In addition, formulations must be tailored such that the heat absorbed during transfer does not decompose the conductor, degrading its adhesion and conductivity. Maintaining the conductivity of a PANI  
35       layer upon thermal transfer is challenging since the heat induced by the laser partially deprotonates the backbone partially driving the polymer into the non-conducting emeraldine form.

Using the present invention, organic conductors can be imaged with high resolution using thermal transfer methods. In particular, specific acids and additives have been identified, which would lead to PANI's that can be imaged using thermal transferring techniques with high resolution and good adhesion to the underlying layer while either maintaining or increasing the conductivity of the transferred layer. The materials disclosed here are appropriate for applications in microelectronics such as gates, sources, drains and interconnects in plastic TFT transistors.

#### DEFINITIONS

By protonic acid is meant an acid molecule containing a proton that dissociates from a counter ion in a solvent.

By carbon nanotubes herein is meant carbon atoms bonded together in a hexagonal pattern to form long cylinders. Nanotubes can also be formed of multiple layers of walls. Carbon nanotubes were discovered about 1991. The nanotubes used herein were obtained from Rice University, Houston, TX, U.S.A.

Preferred solvents herein are selected from the group consisting of xylenes, toluene, cyclohexane, chloroform, or mixture thereof with polar solvent such as isopropanol, 2-butoxyethanol, where the content of the polar solvent is preferably less than 25% by weight, toluene, cyclohexane, chloroform, isopropanol, 2-butoxyethanol and mixtures thereof.

#### DESCRIPTION OF EXPERIMENTAL SETUP

The imaged source and drains in the following examples were obtained using a CREO 3244 Trendsetter exposure unit (Creo Inc. Vancouver, Canada). The system comprises an 81.2-cm long drum of 91-cm perimeter. The 15 cm x 20 cm receiver was taped on to an Al offset plate (71.1 cm x 94.5 cm) at its lower right hand corner. The donor film tightly placed directly on top of the receiver with the emulsion towards the receiver. The offset plate was auto-loaded on to the trendsetter drum and magnetically clamped in position. The donor film was written with an array of 240 5 x 2 micron spots resulting from the splitting of a 20 watt maximum average power infrared diode lasers beam emitting at 830 nm at 1 microsecond pulse width. The drum speed varied to achieve sensitivities of 200 to 550 mJ/cm<sup>2</sup>. The donor films used in the following examples comprised 3 layers: 1) a 4 mil Mylar substrate coated with 2) a thin metal layer heating layer which, in turn, is coated with 3) a solution of the conducting PANI and various additives on top.

### EXAMPLE 1-3

These examples illustrate the effect of added excess acid on the conductivity of a transfer polyaniline layer. The images were obtained using a CREO trendsetter with 5080 DPI (CREO-Scitex, Vancouver, Canada). A Spectrum Trendsetter Exposure Unit, available from Creo Inc. (Vancouver, Canada) exposed the donor elements. The laser average power ranged from 4 to 12 Watts and the drum speed from 100 to 200 RPM. The 0.5 cm by 5 cm solid areas transferred at these laser powers were fabricated using a donor film comprising a 100 Å layer of Ni coated via electron beam deposition by Flex, Inc (Santa Rosa, CA) directly on 400D Mylar to about 40% optical transmission. The layer to be transferred was a 1.3-micron film of L5000 (Ormecon Chemie GmbH and Co. KG, Ammersbek, Germany) PANI coated on to the Ni base. The L5000 solution contains 8.5% solids in equal part of isopropanol and toluene. The L5000 is doped to exhibit high electrical conductivity in the as purchased condition. The manufacture does not disclose the dopant used although it is believed to be p-toluene sulfonic acid. The solution was coated using Meyer rod #6 onto a 15 cm by 20 cm base. Example 1 used the L5000 solution without additives. In Examples 2 and 3, the PANI layer contains 50 % and 100 % excess di nonyl naphthalene sulfonic acid, hereafter referred to as DNNSA. DNNSA is added to the L5000 solution prior to coating on the donor. An excess of 50% implies there are 0.25 moles of sulfur atoms from the excess acid dopant added for each mole of nitrogen in the polyaniline. An excess of 100% implies there are 0.5 moles of sulfur atoms added in the acid dopant for each mole of nitrogen atoms in the polyaniline. Additionally, between 0.05-.05 (weight %) of Zonyl® surfactant, obtained from E.I. duPont de Nemours and Company, Wilmington, DE, was added to the solution. The receiver comprised a 1 micron acrylic latex (55MMA/40BA/3MAA/2GMA where MMA is methyl methacrylate, BA is butyl acryl ate, MAA is methyl methacrylic acid and GMA is glycidyl methacrylate.) coated on to 400D Mylar using a CV® Coater from Dupont, Wilmington, DE, equipped with a #6 Meyer rod. The coating was dried for 3 minutes at a temperature of 50 °C. The 15 cm x 20 cm receiver layer was placed at the bottom right hand corner of a 74.5 cm x 91.1 cm aluminum offset plate. The donor film, with the PANI surface facing the receiver coating, was stretched directly on top of the receiver. The Al offset plate was automatically loaded and positioned using magnetic clamps. To form the patterned image, the laser

beam is focused on to the metal interface. The heat generated begins the decomposition of the organics in the adjacent interfaces, which leads to the transfer of the PANI onto the receiver at the different laser powers. After the exposure is completed, the image on the receiver consists of nine  
5 0.5 cm x 5 cm solid stripes transferred at laser powers ranging from 4 to 12 Watts.

The conductivity of each of the transfer solid stripes was measured using 4-probe method. Thicknesses were determined by a Dektak profilometer. After the film thickness was measured, Ag contacts were  
10 sputtered to a thickness of 4000 Å through an aluminum mask using a Denton vacuum unit (Denton Inc. Cherry Hill, NJ). The film resistivity was measured using the standard 4-probe measurement technique. The current was measured at the two outer contacts. These contacts were separated by 1 " and connected to a Hewlett Packard power supply in  
15 series with an electrometer (Keithley, 617). The voltage was measured at the two inner contacts, separated 0.25" using a Keithley multimeter. The resistivity (in ohm-square) as a function of laser power is shown in Figure 1. The resistivity was calculated as:

$$R=VL/Iwt$$

20 where R is the resistivity, V is the voltage measured at the inner contact, I is the current through the outer contacts, L is the separation between the inner contacts, w is the width of the film and t is the film thickness. The film conductivity, S, is 1/ R.

As shown in Figure 1, the conductivity of the L5000 without excess acid rapidly decreases with increasing laser power. The transferred films without excess acid show extremely low adhesion making it inappropriate for electronic applications. Adhesion was measured by inspection. Poorly adherent transferred layers may not remain on the receiver element after separation of the donor from the receiver after laser exposure.

30 Alternatively, poorly adherent transferred layers may exhibit peeling around the edges. Poorly resolved transferred layers exhibit very irregular edges due to partial detachment. As excess acid is increased (Examples 2 and 3), the film becomes effectively more plasticized so that the adhesion of the transferred layer to the receiver layer is considerably  
35 improved. As shown in Figure 1, PANI with excess acid as an additive transferred in the 6-8 Watts range shows adequate conductivity as well as improved adhesion. Both set levels of excess acid are adequate for electronic applications.

#### Example 4-7

Examples 4 to 7 illustrate the use of excess dodecyl benzene sulfonic acid (DBSA) in L5000 Ormecon PANI to retain electrical conductivity while improving the adhesion of a thermally transferred layer on to a receiver. The procedure for obtaining the donor layer is as previously described in Examples 1-3 with DBSA substituted for DNNSA. The receiver layer, mounting procedure, imaging procedure and conductivity measurements were also as previously described for Examples 1-3.

As shown in Figure 2, excess DBSA generally reduces the film conductivity. Adhesion is improved since the excess acid plasticize the film. Films with 33 % excess acid transferred in the 6-8 Watts regime show improved adhesion and appropriate conductivity. As in Examples 1-3, adhesion was determined by inspection of the transferred layer.

#### Example 8-11

These examples illustrate the effect of added plasticizer and low  $T_g$  (glass transition temperature) organic material as second macromolecules on the adhesion and conductivity of a transferred polyaniline layer.

Plasticizers are materials which when mixed with polyaniline interact with the polyaniline backbone to reduce the mechanical strength of the resulting material. The softer material with plasticizers exhibit enhanced adhesion upon thermal transfer. Appropriate plasticizers should be soluble in the organic solvent used to dissolve the polyaniline. Appropriate solvent include xylenes, toluene, cyclohexane, chloroform, isopropanol, and 2-butoxyethanol. Examples of appropriate plasticizers are alkyl or aryl esters, alkyl or aryl phosphates, and alkyl or aryl sulfonamides. Second macromolecules are waxes or polymers which raise the average decomposition temperature of their mixture with polyaniline. A transfer layer containing polyaniline is subject to heat during the thermal transfer process. Addition of a high decomposition temperature material to the polyaniline serves to absorb some of the heat generated during the transfer process, thus protecting the polyaniline from decomposition. Appropriate second macromolecules should be soluble in the organic solvent used to dissolve the polyaniline. Examples of appropriate second macromolecules are polyacrylate, polystyrene, ployester, polystyrene methyl methacrylate, co-polymers of ethylene/n-butyl acrylate/carbon monoxide such as Elvaloy HP441®, and chlorinated paraffin such as

Chlorowax 50®. The low glass transition material is Chlorowax 50 hereafter referred to as CW50 (Occidental Chemical Corporation, Dallas, TX). The plasticizer is di-phenyl phthalate (dPP) (Aldrich, Milwaukee, WI). The procedure for obtaining the donor layer is as previously described in Examples 1-3 with excess DNNSA addition omitted. Instead CW50 or CW50 and dPP were added to the L5000 solution as described in Table 2. The receiver layer, mounting procedure, imaging procedure and conductivity measurements were also as previously described for Examples 1-3.

Table 2

	Control	Ex. 8	Ex. 9	Ex. 10	Ex. 11
L5000 (8.5% )	50 gr.	45 gr.	40 gr.	35 gr.	40 gr.
CW50		0.425	.85	1.275	.425
dPP					.425
L5000/CW/dPP	100/0/0	90/10/0	80/20/0	70/30/0	80/10/10

The conductivity of the transferred solid strips as a function of the laser transfer power is shown in Figure 3.

A minimum average laser power of 7 Watts was required to obtain adequate transferred layer adhesion and resolution. As shown in Figure 3, the conductivity is slightly reduced as the CW50 concentration reaches 30%. The adhesion of the transferred films in Ex. 10 and Ex .11 on to the receiver was excellent. However, Example 11 with only slightly less adhesion than Ex. 10 exhibited conductivity larger than 1 S/cm. This value is sufficient for electronic applications such as sources and drains in plastic transistors. Example 11 is a preferred embodiment of this invention

#### Example 12-17

These examples illustrate the effect of added plasticizers on the adhesion and conductivity of a transfer polyaniline layer. The procedure for obtaining the donor layer is as previously described in Examples 1-3 with excess DNNSA addition omitted. Instead dPP or di-butyl phthlate (dBP) was added to the L5000 solution as described in Table 3 prior to coating on the donor element. The receiver layer, mounting procedure, imaging procedure and conductivity measurements were also as previously described for Examples 1-3.

Table 3

	control	Ex 12	Ex 13	Ex 14	Ex 15	Ex 16	Ex 17
L5000 (8.5% )	50 gr.	45 gr.	40 gr.	35	45 gr.	40 gr.	35 gr.
dBP					0.425	0.85	1.275
dPP		0.425	0.85	1.275			
L5000/dBP/ dPP	100/0/ 0	90/0/ 10	80/0/ 20	70/0/ 30	90/10 /0	80/20 /0	70/30 /0

5 A minimum average laser power of about 7 Watts is required to transfer the layer with adequate adhesion and resolution. As shown in Figure 4, the conductivity is significantly reduced when dBP concentration reaches 30%. In contrast, similar concentrations of dPP result in sufficient adhesion without degradation of the conductivity. The adhesion of the transferred films in Example 14 as well as the resulting conductivity was  
10 sufficient for electronic applications such as sources and drains in plastic transistors. Example 14 is a preferred embodiment of this invention.

Examples 18-21

15 These examples illustrate the effect of adding high decomposition temperature polymers as binders to polyaniline transferred layers. The procedure for obtaining the donor layer is as previously described in Examples 1-3 with DNNSA omitted. Instead, polystyrene methyl methacrylate (PSMMA) or Elvaloy @ 441 (hereafter HP441) were added to the L5000 solution prior to coating on the donor element. The receiver layer, mounting procedure, imaging procedure and conductivity  
20 measurements were also as previously described for Examples 1-3. The polystyrene methyl methacrylate (PSMMA) was obtained from Polyscience and the Elvaloy 441 is a copolymer of ethylene/n-butyl acrylate/carbon monoxide from DuPont, Wilmington DE.



Table 4

	Control	Ex. 18	Ex. 19
L5000 (8.5% )	50 gr.	40 gr.	40 gr.
PSMMA			0.85
HP 441		0.85	
L5000/HP441/PSMMA	100/0/0	80/0/20	80/20/0

5       The conductivity of the solid strips as a function of the laser transfer power is shown in Figure 5.

      A minimum average laser power of about 7 Watts is required to obtain adequate adhesion and resolution in the transferred layer. As shown in Figure 5, the conductivity is reduced below 1 S/cm at higher laser powers. In order to obtain adequate adhesion and high resolution  
10   imaging for material represented by Examples 18 and 19, a plasticizer should be added in addition to the binders described.

      Figure 6 shows the effect of addition of PSMMA (Example 20) and PSMMA with 5%dBP (Example 21) to L5000 on the conductivity of the untransferred material. The films that were made were measured using a  
15   point probe. The conductivity changes very slightly with considerable amounts of PSMMA and PSMMA with 5% dBP. The conductivity of the same films measured after laser transfer decreases rapidly as a function of the laser power used in the transfer process. Despite the decrease, the conductivity is adequate for use in electronics.

#### Examples 22-33

20       These examples show the effect of the addition of carbon nanotubes and excess DNNSA on laser transferred films of PANI. Addition of DNNSA is believed to increase the film adhesion to the receiver while the addition of carbon nanotubes increases the conductivity.

25       In carbon nanotubes, the carbon atoms are bound together in a hexagonal pattern to form long cylinders 1.2 nm in diameter. Nanotubes can also be formed with multiple layers of walls. They have good thermal and electrical conductivity. The nanotubes used in Examples 22 to 33 were manufactured by Rice University, Houston, TX, U.S.A. through the  
30   pulsed laser vaporization of a metal/carbon target in a furnace at 1100 °C. This produces a sooty material, which is about 50% single-walled nanotubes. The rest of the material is amorphous carbon and residual

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catalyst particles. The main impurity is leftover Ni/Co catalyst particles. Most tubes are between 0.2 and 2 microns in length

The polyaniline (PANI) used was prepared through emulsion polymerization following the procedure outlined in P. J. Kinlen, US Patent 5,863,465. Dinonylnaphthalene sulfonic acid (DNNSA) was used as the dopant. The resulting material is hereafter referred to as PANI-DNNSA. The addition of DNNSA was controlled such that the moles of the sulfur atoms from the acid equals the moles of nitrogen atoms in the backbone of the PANI. This was confirmed by elemental analysis studies after washing, separating and drying of the resulting PANI-DNNSA.

The dispersion of carbon nanotubes in PANI-DNNSA was performed with an acoustic Dukane sonicator with a horn probe using the following procedure. For Example 22, 59 mg Rice Laser carbon nanotubes and 19.03 g xylene were mixed in a 2 oz. bottle. The mix was dispersed for 10 minutes with the horn probe submerged in the mix at a depth such that a stable mixing vortex was observed. 5.90 g of PANI-DNNSA in xylene solution with a 32.9% solid content was added to the mixture. The resulting mixture was dispersed for additional 5 minutes during which time the bottle was shaken two times in order to rinse the carbon nanotubes off the walls of the bottle. The resulting slurry at 8% total solids was then coated as a 1-micron film using a Meyer rod #10. The film contains 3% NT and 97% polyaniline after drying.

For Examples 23, 60 mg Rice Laser carbon nanotubes and 19.01 g xylene were added to a 2 oz. bottle. The mix was dispersed for 10 minutes with the horn probe submerged in the mix to a depth such that a stable mixing vortex was observed. 5.90 g of PANI-DNNSA with 32.9% solid content were added to the mixture. The resulting mixture was dispersed for additional 5 minutes during which time the bottle was shaken two times in order to rinse the carbon nanotubes off the walls of the bottle. 0.48 g of Nacure 1051 (50% by weight DNNSA in 2-butoxyethanol from King Industries) was then added to the mixture and mixed by shaking for two minutes. The resulting slurry at 8% solids was then coated as a 1-micron film using a Meyer rod #10. The film after drying contains 3% NT and 97% polyaniline. There is a 15% excess of DNNSA. For Example 24, the same procedure as Example 23 was used although with a 0.78 g addition of Nacure. This results in a 25% excess of DNNSA. Table 5 summarizes the composition of these examples.

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Table 5

Example	Ex.22	Ex. 23	Ex. 24
PAni-DNNSA 101261-130 (g)	5.90	5.90	5.90
Carbon nanotube (mg)	59	60	61
Xyleness (g)	19.03	19.01	18.99
Nacure 1051 (g)	0	0.48	0.78
Excess DNNSA (%)	0	15	25

5 Figure 7 below shows the conductivity of solid transfer films as a function of laser power. The imaging and conductivity measurements were performed as described Examples 1-3. The adhesion of the materials in Examples 23 and 24 is adequate. As seen in Figure 7, the conductivity of the transferred film is adequate for average laser power above about 5 watts. Example 24 is a preferred embodiment of this  
10 invention.

Examples 25 to 27 demonstrate the effect of addition of carbon nanotubes on the conductivity of PANI-DNNSA without excess acid. For Examples 25, 26, and 27, the same procedure was followed as outlined for Example 22. This resulted in films with 1, 2, and 3% by weight carbon  
15 nanotubes, respectively. Table 6 summarizes the compositions of these examples.

Table 6

Example	Ex.25	Ex. 26	Ex. 27
PANI -DNNSA	9.01	6.72	5.90
Carbon nanotube (mg)	33	45	59
Xyleness (g)	15.94	18.26	19.03

20 The carbon nanotube/PANI-DNNSA solutions at 0, 1, 2 and 3% by weight carbon nanotubes concentrations were coated onto the Ni base previously described using a #10 Meyer rod and imaged using the CREO following the procedure described in Example 1.

25 When the adhesion and conductivity of the transfer film is balanced high-resolution images can be obtained. The films of Examples 24

through 27 all exhibit adequate conductivity, adhesion and resolution. Example 27 is a preferred embodiment of this invention.

The transfer of the conducting transfer layer by thermal imaging allows for very accurate control of line widths and channel widths.

5 Figure 9 shows the conductivity of 100 microns wide lines, 1250 microns in length. The sets of 15 lines were measured using a 4-probe technique as well. The contacts as well as the lines were imaged directly into a pattern suitable for a 4-probe measurement. The voltage and current to the contact lines were applied under the microscope using mini-manipulators  
10 with needle tungsten probes that could be exactly positioned on the line at the end. The patterns were transferred at specific laser powers and their conductivity measured.

The materials in Examples 28, 29 and 30 correspond to the materials used to Examples 25, 26, and 27. Examples 31, 32 and 33 were  
15 dispersed using the same procedure as Example 24. Examples 31, 32 and 33 all have 25% excess acid, but the carbon nanotube concentrations are 1, 2, and 3% by weight, respectively. Table 7 summarizes the composition of the materials.

20 Table 7

Example	Ex.31	Ex. 32	Ex. 33
PAni-DNNSA	9.00	6.70	5.90
Carbon nanotube (mg)	30	44	61
Xyleness (g)	15.98	18.25	18.99
Nacure 1051 (g)	1.19	0.89	0.78
Excess DNNSA (%)	25	25	25

Figure 9 shows that while excess acid improved the adhesion of the transfer material to the receiver, the conductivity was frequently  
25 decreased. The conductivity generally increases with increasing carbon nanotube concentration. However, the addition of the carbon nanotubes tends to decrease the adhesion of the film, counteracting to some degree the addition of the acid. In order to obtain a transferred film with appropriate adhesion and conductivity, the ratio of acid and carbon  
30 nanotubes must be balanced. Example 33 with 3% nanotubes and 25% excess DNNSA is best mode of this invention, representing the desired balance.

CLAIMS

What is claimed is:

1. A composition comprising:

- 5 a) A polyaniline polymer, doped with an organic protonic acid with 3 to 30 carbons, such that there are between 0.3 and 2.0 acid molecules for each nitrogen in the polyaniline polymer backbone, said polymer optionally doped with excess organic protonic acid with 3 to 30 carbons such that there are between 0.15 and 1 molecules of the excess organic protonic acid for each nitrogen in the polyaniline;

10 the composition further comprising one or more components selected from the group of:

- b) Surfactant at a concentration of between 0.05% and 0.5% by weight;
- 15 c) plasticizer at a concentration of between 1% and 30% by weight; and
- d) a second macromolecule at a concentration between 1% and 30% by weight; and

20 wherein the doped polymer of (a) comprises not less than about 70% by weight of the solids in the composition.

2. The composition of Claim 1 further comprising carbon nanotubes at a concentration between 0.5% to 13% by weight.

3. The composition of Claim 1 wherein the plasticizer is soluble in an organic solvent used to dissolve the polyaniline.

25 4. The composition of Claim 1 wherein the plasticizer is selected from the group consisting of alkyl or aryl esters, alkyl or aryl phosphates, and alkyl or aryl sulfonamides.

5. The composition of Claim 1 wherein the second macromolecule is a wax or polymer.

30 6. A process comprising:

- a) coating the composition of Claim 1 or Claim 2, in a solvent, on a transparent donor element
- b) contacting the transparent donor element with a receiver element such that the coating lies between the transparent donor element and the receiver element; and
- 35 c) irradiating the coating through the transparent donor element with a laser to transfer the coating on the transparent donor element to the receiver element.

7. The process of Claim 6 wherein the solvent is selected from the group consisting of xylenes, toluene, cyclohexane, chloroform, or mixture thereof with polar solvent such as isopropanol, 2-butoxyethanol , where the content of the polar solvent is preferably less than 25% by weight., toluene, cyclohexane, chloroform, isopropanol, 2-butoxyethanol and mixtures thereof.

8. The process of Claim 7 where the laser irradiation forms a pattern.

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TITLE

## LASER PRINTING OF CONDUCTIVE POLYANILINE WITH ADDITIVES

ABSTRACT

5 Additives to conductive polyaniline are described which enhance  
adhesion and resolution of laser printed films while retaining adequate  
electrical conductivity. The conductive polymer films are useful in printing  
conductive portions of thin film transistors such as sources and drains.  
Additives include surfactants, second macromolecules, plasticizers, and  
excess sulfonic acids.

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BCS/dmm

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Figure 1

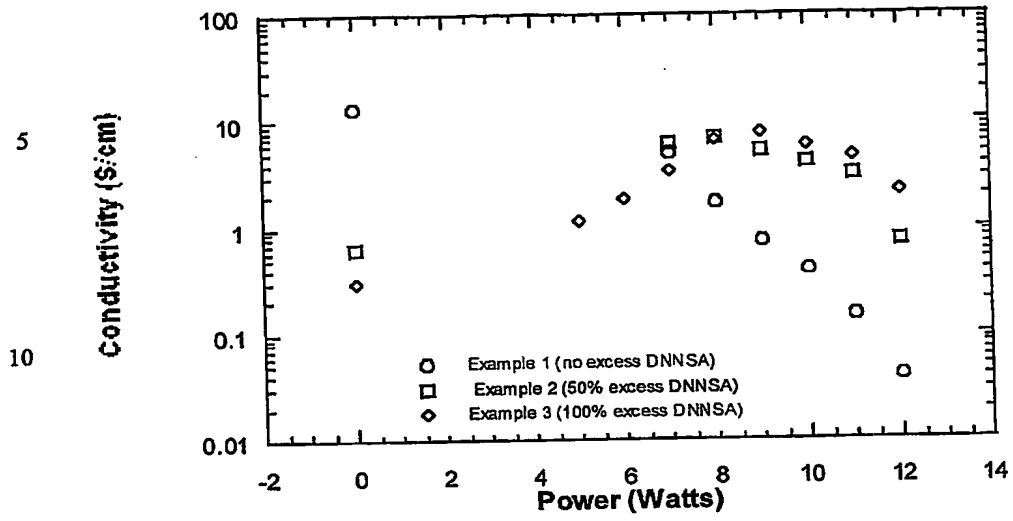


Figure 2

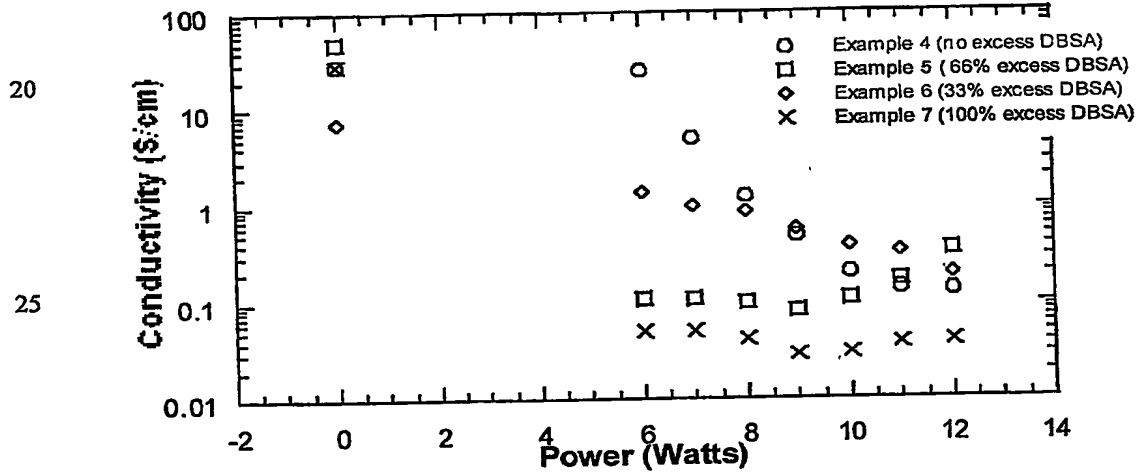




Figure 3

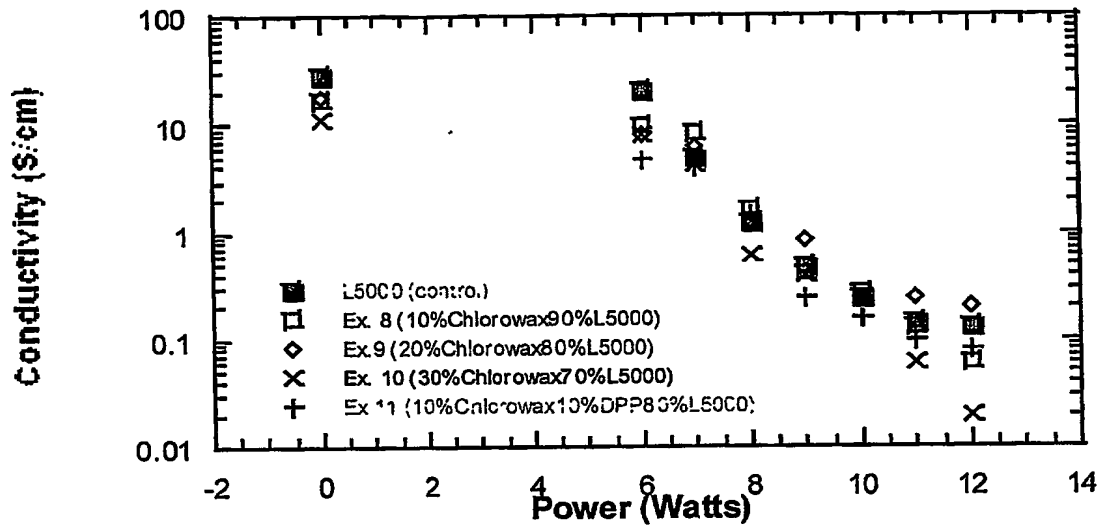
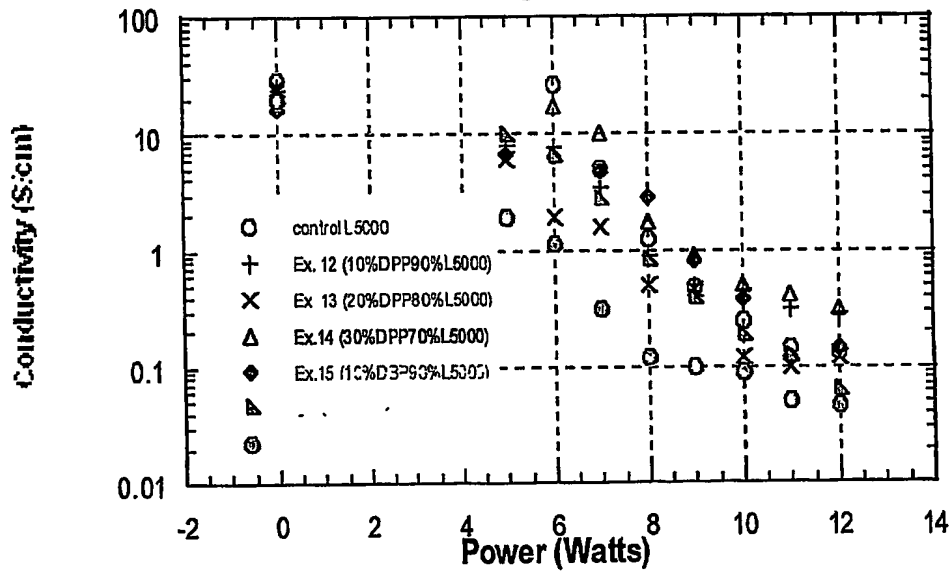


Figure 4



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Figure 5

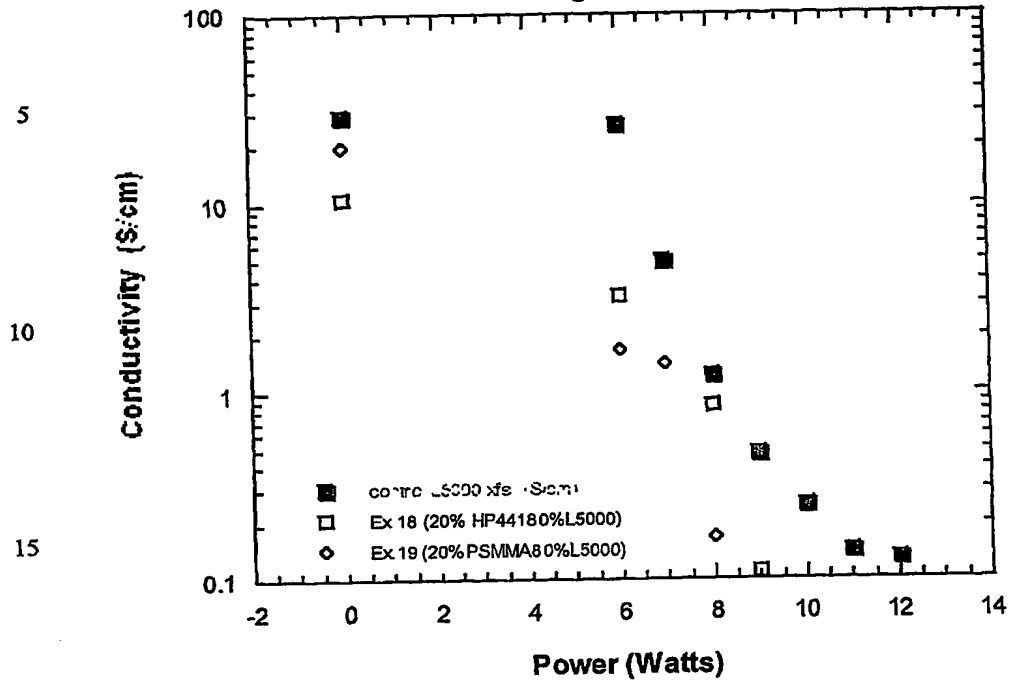


Figure 6

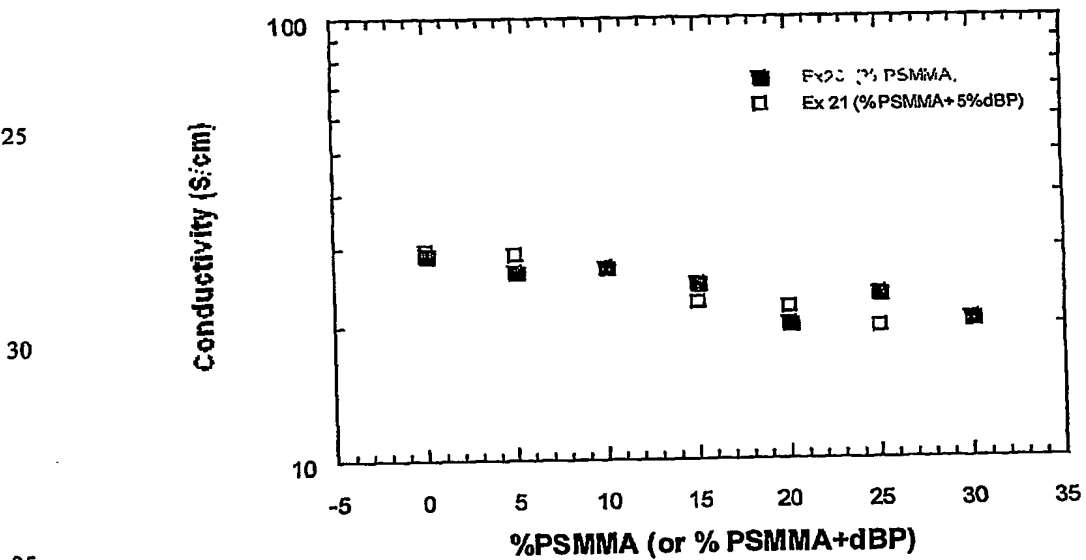


Figure 7

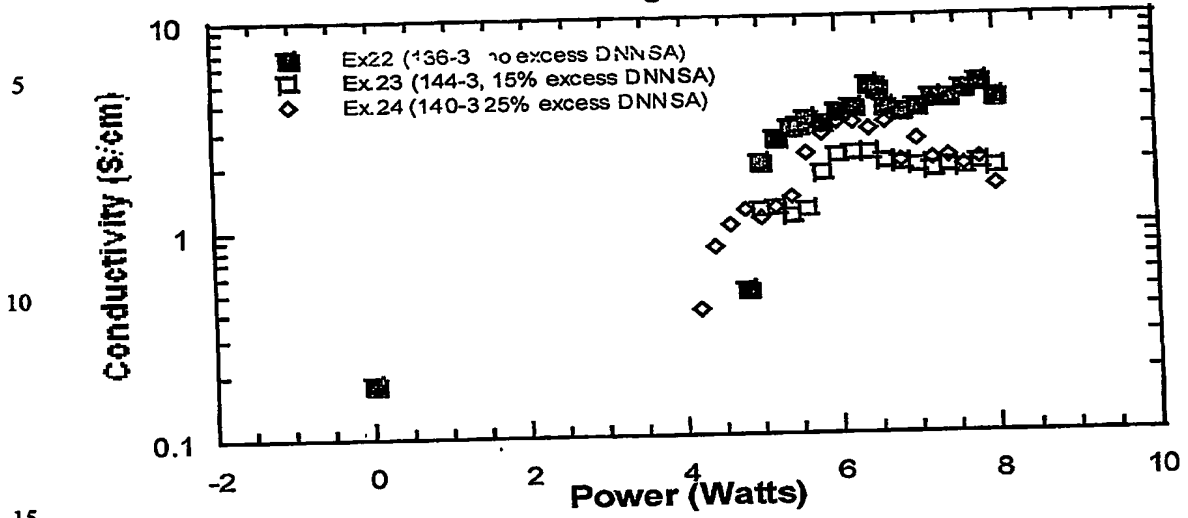


Figure 8

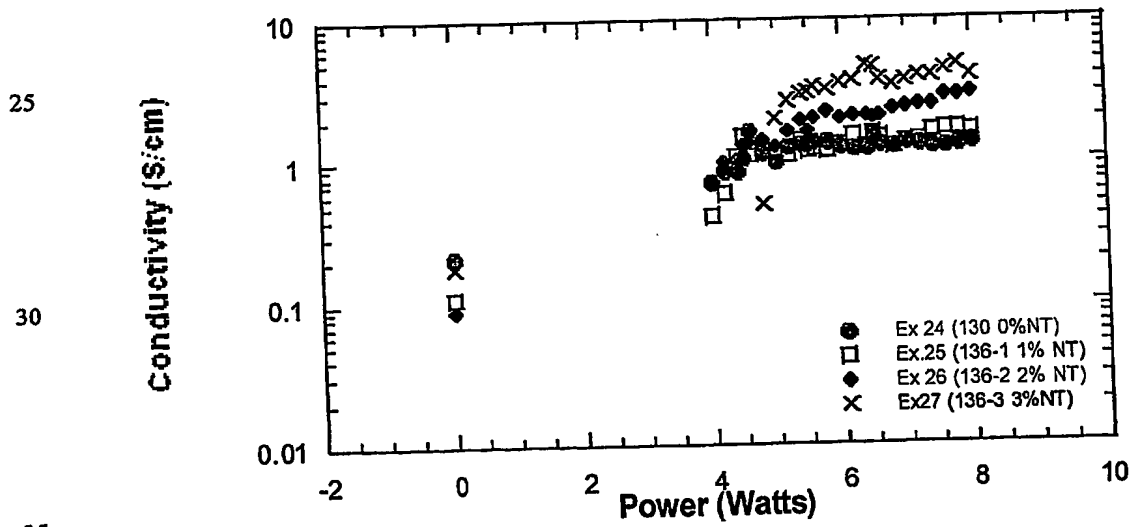


Figure 9

